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14. ABSTRACT
Silica (SiO2) glass is one of the essential materials in human civilization for making household items, window panes, lenses and optical fibers. An important reason for its wide adaptation is its formability near the glass-transition temperature (Tg > 1100• C). SiO2 glass at room temperature, however, is usually brittle due to fracture instability. But when the "brittle" glass is confined in extremely small dimensions at tens of nanometres, the nature of flow and fracture may change. Newest experiments performed at Sandia Center for Integrated Nanotechnologies (CINT) show that glass nanowires with diameters less than 20 nm can become ductile at room temperature, with surprisingly large tensile plastic elongations up to 18% (Luo et al., submitted for review in Nature). Remarkably, these ductile glass nanowires also possess high flow strengths, and are thus much more energy-absorbing and damage-tolerant than

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FIRST-PRINCIPLES MODELING OF
MECHANICS AND CHEMISTRY OF MATERIALS
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Abstract

Silica (SiO_2) glass is one of the essential materials in human civilization for making household items, window panes, lenses and optical fibers. An important reason for its wide adaptation is its formability near the glass-transition temperature ($T_g > 1100°C$). SiO_2 glass at room temperature, however, is usually brittle due to fracture instability. But when the "brittle" glass is confined in extremely small dimensions at tens of nanometres, the nature of flow and fracture may change. Newest experiments performed at Sandia Center for Integrated Nanotechnologies (CINT) show that glass nanowires with diameters less than 20 nm can become ductile at room temperature, with surprisingly large tensile plastic elongations up to 18% (Luo et al., submitted for review in *Nature*). Remarkably, these ductile glass nanowires also possess high flow strengths, and are thus much more energy-absorbing and damage-tolerant than expected. Atomistic modeling indicates that the unexpected ductility is due to the development of a surface affected zone in the nanowires, which enhances ductility by producing more bond-switching events per irreversible bond loss.

Introduction

Silica glass is well known for its brittle failure at relatively low tensile loads of the order of few hundreds MPa. The tensile strength of glass fibers however drastically increases with decreasing diameter, which was attributed by Griffith to the decreasing probability for finding surface imperfections. Tensile strengths of 10-20 GPa can now be reached in sub-micron silica glass fibers [1]. These tensile strengths are close to estimates of the theoretical strength $E/\pi \approx 23$ GPa. Although the theoretical strength and the elastic constants[2] change with decreasing sample size, up to now no change in the failure mode has been reported: structures with dimension > 100 nm are reported to fail in a brittle manner [1, 3]. There are now however some experimental evidence that silica glass might be able to deform plastically under tension and thus show an increased toughness. As discussed by Bruckner, the fracture energy in experiments is higher than expected from elasticity theory for perfectly brittle fracture. Fracture surface energies calculated from the critical stress intensity factor and measured from surface tension differ by one order of magnitude. This difference could be attributed to plastic deformation at the crack tip. Furthermore, glass fibers embedded in a matrix show at high stresses deviations from the linear stress strain curve indicating non-elastic deformations. Recent AFM studies of fracture surfaces in glass indicated that during slow crack growth, nanoscale cavities can form in front of the crack tip, and thus "glass would break like a metal, but at the nanometer scale" [4, 5]. This possibility of crack tip plasticity at room temperature in silicate glasses is however subject of controversy[6, 7].

Simulation Methods

Molecular dynamics simulations of uniaxial tensile deformation at a constant strain rate of 10^9/s at 300K were performed on two amorphous silica samples: a wire of diameter d=4.5 nm and length l=11nm with periodic boundary conditions along the wire axis, and a rectangular sample of dimensions 5.5x5.5x11 nm^3 under periodic boundary conditions in all directions. The atomic interaction potential is the original silica potential by Vashishta et al.[8] cut off, shifted and smoothed at r_c=0.8 nm. The bulk sample was constructed from a crystobalite crystal following the stepwise cooling procedure laid out in [9] while maintaining zero pressure, following an energy minimization and subsequent equilibration at 300K, again at zero pressure. The so obtained sample has a density of ρ=2.42 (2.2) g/cm^3 and 0K elastic constants

(experimental values in brackets): Young's modulus E=109 (73-74) GPa, shear modulus G=44 (31) GPa, and bulk modulus B=61 (31-38) GPa, leading to Poisson's ratio of ν=0.21(0.17-0.18). From the relaxed sample the wire was cut out, taking care that the overall charge neutrality was maintained. The wire was again relaxed and equilibrated at 300 K. MD simulations were carried out using the DLPOLY package[10] using the Berendsen thermostat with a time step of 1 fs and the smoothed particle mesh Ewald method for calculating the coulombic interactions (real space cut-off 1.05 nm and accuracy of 10^{-6}). In the bulk simulations, the length of the box vectors orthogonal to the tensile direction is controlled by the Berendsen barostat to maintain uniaxial stress conditions.

Results

The stress strain response of the wire and the bulk sample are shown in Fig.1. Both samples are initially free from any larger flaws. The wire shows an earlier deviation from the elastic slope and lower stress levels compared to the bulk sample. After a plastic region (between about 10 and 15 % strain) the bulk sample fails whereas the wire shows a large drop in the stress but is not fully fractured at 30% strain.
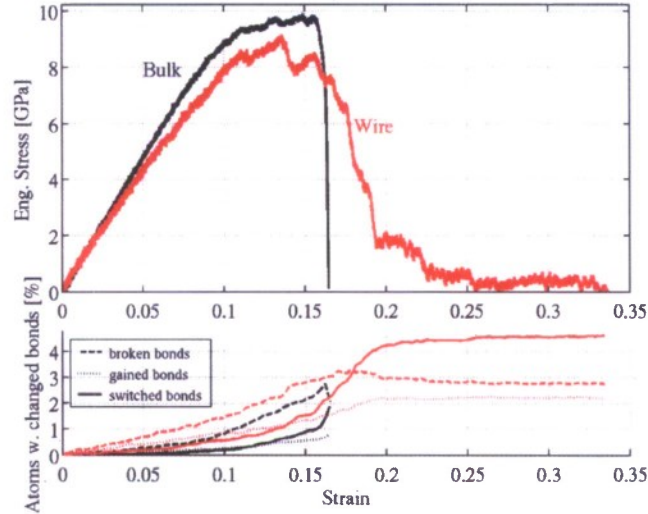

Figure 1: Engineering stress-strain curve for the tensile simulations together with the percentage of atoms which have changed their bonding topology compared to the reference configuration without strain.

Analysis of the atomic configurations shows that the wire is not entirely fractured, but that a connecting ligament was formed during the fracture process, see Fig. 2. In contrast to the fracture plane of the bulk sample, the fracture surface of the wire is inclined with respect to the tensile direction. This is an indication that the failure of the wire has an additional shear component and does not proceed purely by cleavage as in the case of the bulk sample.

An analysis of the evolution of the bonding topology shows that in the wire proportionally more atoms are involved in the deformation process than in the bulk. In particular, in the case of the wire, proportionally more atoms have switched their bonds rather than lost their bonding partner compared to the bulk case. The ratio between atoms which in the plastic region (between 10-15% strain) have lost a bond and atoms which have switched bonds is about 2-2.5 for the wire compared to 2.5-4 in the bulk. When the atoms with added bonds are included in the calculation, the ratio of atoms with broken bonds to atoms which have either gained a bond or switched a bond before the stress drop is about 1 for the wire and between 1.5 and 2 for the bulk. The existence of a free surface thus significantly reduces the relative amount of breaking bonds. The fact that we have microplasticity also for the bulk sample even well within

the elastic region could be caused by the relatively high number of atoms (2.3%) which have imperfect coordination.
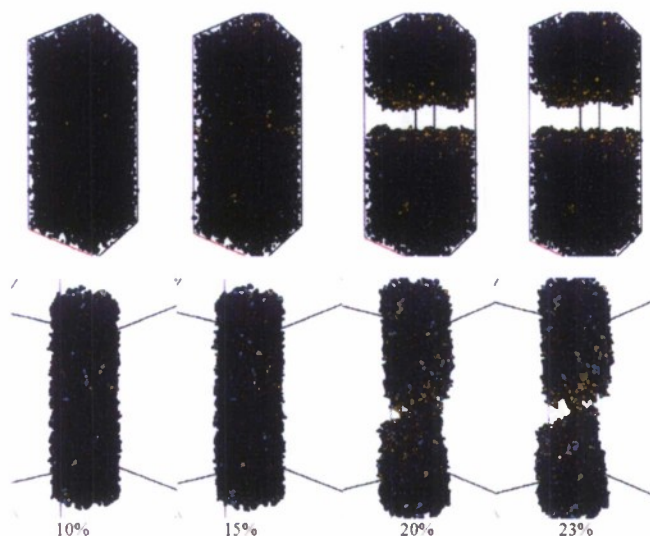
Figure 2: Snapshots from the bulk sample and the wire at different strains. The atoms are colored according to the to changes of their bonding topology: dark blue atoms have exactly the same neighbors as in the strain free initial configuration, light blue atoms have gained a bond, yellow atoms have switched bonding partners while maintaining the same coordination number, red corresponds to broken bonds.

Discussion

At very small system sizes failure is no longer controlled by the (catastrophic) propagation of pre-existing flaws but by the nucleation of a crack like defect. This is reflected by the high tensile stresses - close to the theoretical strength sustained by the silica sample in the experiment as well as in the simulations.

In the present simulations, both the "bulk" sample and the wire are of comparable size and free of initial defects. Moreover, as the wire has been cut out from the bulk system, it shares a similar internals structure as the bulk. The MD bulk sample clearly does not represent the actual flaw distribution in real bulk amorphous silica. The use of periodic boundary conditions however models the topological constraints the silica network would be subjected to within the bulk of a flawless glass.

The high stresses which the defect free glass can sustain lead to a limited plastic deformation which is usually not seen in experiments where such high tensile stresses can only be reached for sub-micron wires.

The effect of the free surface on the deformation in the simulations can be rationalized by realizing that although flaws and cracks nucleate preferentially at the surface, plasticity is also increased at the surface. In fact, most of the observed bond switching processes in the simulation of the wire take place at the surface. Bond switching and bond formation change the network topology and thus correspond to a local plastic event. The reasons for the increased bond switching at the surface are twofold: first, the missing bonding constraints at the surface lead to an increased flexibility of the silica tetrahedra. These can rotate to accommodate strain (see Fig. 3), but can thereby also bring their non-bridging oxygen close to under-coordinated silicon atoms. Secondly, the presence of under-coordinated atoms catalyses bond switching and thus plastic deformation. This could also explain the enhanced ductility of irradiation-damaged silica. The enhanced bond formation and bond-switching at the surface thus

can heal nucleated flaws at the surface before they become critical and propagate through the sample leading to cleavage of the wire.

In the following the fundamental deformation mechanisms in silica glasses are described in more detail. In all pictures the atoms are colored according to their coordination number, with under-coordinated silicon atoms being green and non-bridging oxygen atoms colored in turquoise.

Tetrahedral reorientation:

In addition to elastic deformation by bond elongation and bending, partly un-bonded silica tetrahedral can rotate and thereby change the Si-O-Si from acute to oblique or vice-versa, see Fig. 3. This deformation preserves the bonding topology but as the new configuration represents a local energy minimum, it will not be linearly reversible. Such a deformation is therefore not elastic but in-elastic.
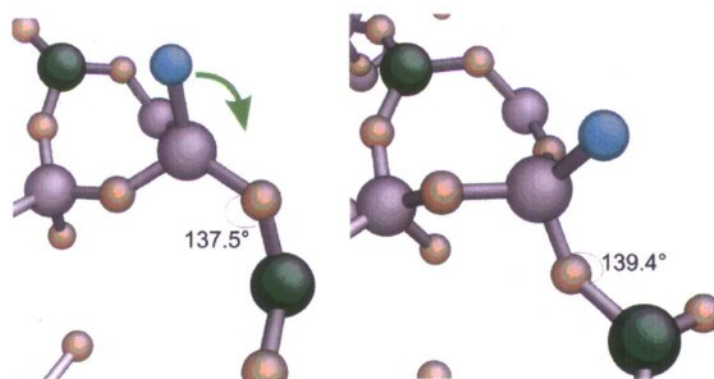
Figure 3: Snapshots of the process of tetrahedron rotation at the surface of the wire (4% strain, time between snapshots 5 ps).

Bond breaking and bond formation:

All fundamental mechanisms of plastic deformation and fracture involve in one way or the other the breaking of bonds. Fig. 4 shows how the local breaking of Si-O bonds between the Atoms A and B and C and D leads to a relatively large plastic deformation. Local bond breaking does not necessarily lead to fracture of the sample. In the back plane of the same figure one can see an example of bond formation between an under coordinated (green) Si atom and a turquoise O atom.
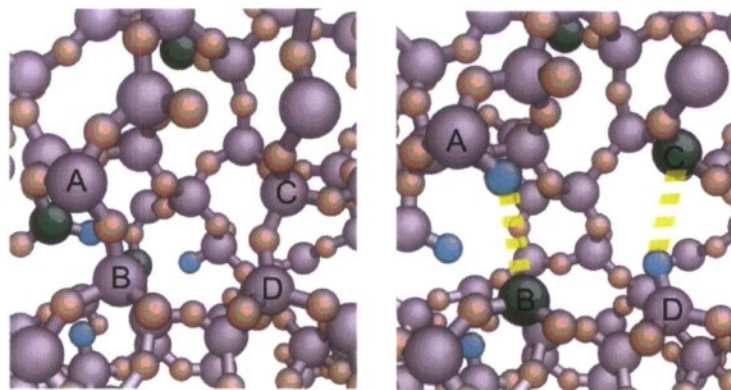
Figure 4: Example of bond breaking. In this case two bonds break simultaneously (shown by the dashed yellow lines), while in the back plane a new bond is formed (Wire, 16.7% strain, time between snapshots 2.5 ps)
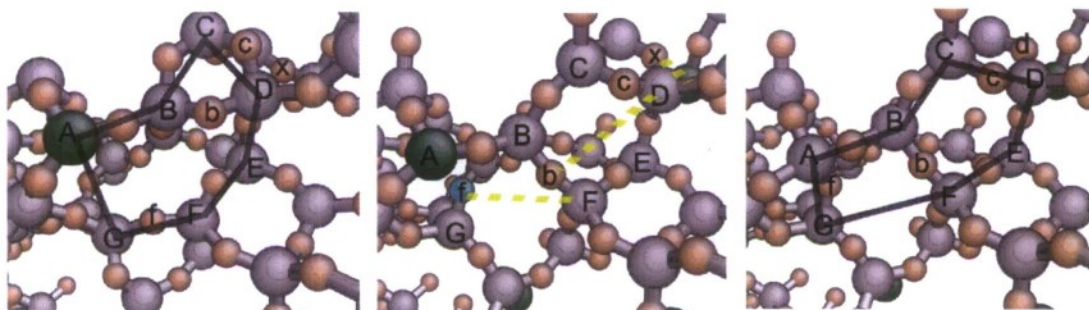
Bond switching:

Switching of bonds can be defined as *correlated* bond breaking and subsequent bond formation. Contrary to crystals where bond switching takes place during the passage of a dislocation, bond switching in silica glass is hard to imagine topologically without pre-existing defects (dangling bonds), or at least the creation of a defect. Bond switching is therefore catalyzed by existing defects and thus favored at surfaces. Shown in Fig. 5 is a simple example for bond switching: the bond between B and a is broken to form a new bond between B and the dangling c. As can be seen this leads to a deformation of the network, which in principle could be reversible upon unloading, as long as a has not found a new bonding partner.
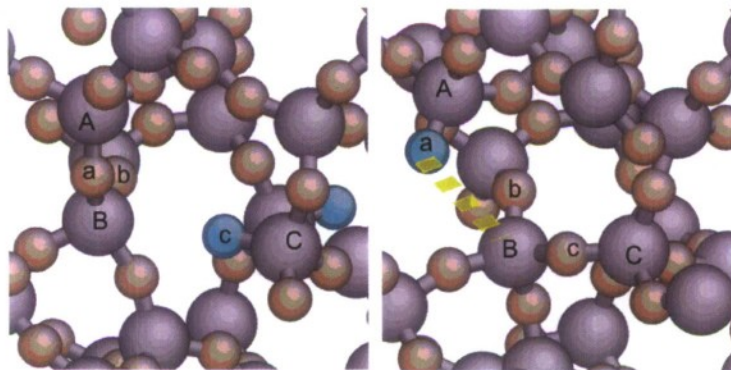
Figure 5: Example of simple bond switching, catalyzed by the non-bridging oxygen c. (bulk simulation, 9% strain, time between snapshots 2.5 ps)

Fig. 6 shows a more complicated example of correlated atomic motion (wire, 10% strain, time between snapshots 2.5 ps): The bond between f and F is broken and replaced by the bond between b and F. The bond between b and D is in turn replaced by the bond between D and x, which generates an under coordinated silicon atom. Subsequently the dangling bonds at f and A form a new bond. As indicated with the solid line, this bond switching leads to a significant shape change of the network formed by the atoms involved in this process. This region is thus akin to a shear transformation zone (STZ).

Figure 6: Example of complex bond switching.

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Ju Li, Erik Bitzek, Ji Feng, Liang Qi, Amit Samanta

Presentations

Invited talk, School of Materials Science and Engineering, Shanghai Jiao Tong University, June 10, 2009.

Invited talk, International Workshop on Size Effect on Materials Mechanical Behavior, Beijing, May 24 - 26, 2009.

Invited talk, Center for Integrated Nanotechnologies (CINT), Sandia National Laboratories, Albuquerque, New Mexico, May 7, 2009.

Invited talk, Othmer-Jacobs Department of Chemical and Biological Engineering, Polytechnic Institute of NYU, Brooklyn, New York, May 4, 2009.

Invited talk, MRS Spring Meeting, symposium *Probing Mechanics at Nanoscale Dimensions*, San Francisco, April 13-17, 2009.

Invited talk, Shanghai Institute of Ceramics, March 10, 2009.

Invited talk, TMS 2009 Annual Meeting & Exhibition, San Francisco, February 15-19, 2009.

Keynote talk (40 min), "Tensile Ductility of Nanostructured Metals," Plasticity 2009, St. Thomas, U.S. Virgin Islands, January 3-8, 2009.

Invited talk, Workshop on Mechanical Behaviors of Micro/Nano Materials, XiAn Jiao Tong University, December 30-31, 2008.

Two invited talks, National Sun Yat-sen University, Kaohsiung, Taiwan, December 13-21, 2008.

Invited talk, Georgia Institute of Technology Woodruff School of Mechanical Engineering Seminar, Oct. 23, 2008.

Invited talk, Dislocations 2008, Hong Kong, Oct. 13-17, 2008.

Invited talk, Brown University Joint Materials/Solid Mechanics Seminar, September 12, 2008.

Invited talk, "Plasticity in amorphous and nanocrystalline metals," Gordon Research Conference on Thin Film & Small Scale Mechanical Behavior, Colby College, Maine, July 27 - August 1, 2008.

Two invited lectures, Workshop on Multi-Scale Modeling of Moving Interfaces in Materials, Katholieke Universiteit Leuven, Belgium, July 2-4, 2008.

Invited talk, 2nd International Conference on Heterogeneous Materials Mechanics (ICHMM-2008), Huang-Shan, China, June 3-8, 2008.

Invited talk, International Workshop on *in situ* Electron Microscopy in Advanced Materials Research, Beijing, May 31 - June 2, 2008.

Invited talk, NIST 2008 Diffusion Workshop, Gaithersburg, Maryland, May 12-13, 2008.

Invited talk, TMS 2008 Annual Meeting & Exhibition, New Orleans, March 9-13, 2008.

Invited talk, International Workshop on Small Scale Plasticity, Braunwald, Switzerland, September 5-8, 2007.

Publications

1. L. Lu, M. Dao, T. Zhu and J. Li, "Size dependence of rate-controlling deformation mechanisms in nanotwinned copper," *Scripta Mater.* **60** (2009) 1062-1066.

2. T. Zhu, J. Li, S. Ogata and S. Yip, "Mechanics of Ultra-Strength Materials," *MRS Bulletin* **34** (March 2009) 167-172.

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